Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"Two Crystallised, Isomeric d-Fructose-Penta-acetates"*. By Prof. Dr. F. M. JAEGER.

(Communicated in the meeting of June 30, 1917.)

§ 1. Nine years ago [1]) the crystallonomical character was described of a *d-Fructose-tetra-acetate* (rupt : 132° C.), prepared by Dr. D. H. BRAUNS. The compound is *monoclinic-sphenoidical*, with the parameters: $a : b : c = 1,3463 : 1 : 1,5733$, and $\beta = 52°12'$. A short time ago HUDSON and BRAUNS [2]) succeeded in obtaining two isomeric crystallised *d-Fructose-penta-acetates*, whose form-analogy is strikingly evident, as will be clear from what follows.

Both *penta-acetates* possess the same cycle of atoms in their molecules, as is proved by the fact that they both are obtainable from *d-Fructose-tetra-acetate*, namely the α-modification by means of $ZnCl_2$ and *acetic acid-anhydride*, the β-modification by means of strong *sulphuric acid* and *acetic-acid-anhydride*.

§ 2. I. *α-d*-FRUCTOSE-PENTA-ACETATE.

The substance melts at 70° C.; its specific rotation at 20° C. is: $[\alpha]_D = = + 34°,75$ in chloroform-solution. Its taste is a little bitter, and it crystallises from a mixture of alcohol and chloroform in prismatic crystals which are reproduced in fig. 1.

Rhombic-bisphenoidical.

$a : b : c = 0,4946 : 1 : 0,3349$

Fig. 1.
ν d-Fructose-penta-acetate.

Forms observed: $m = \{110\}$, predominant, and $b = \{010\}$, appreciably smaller. The prism-zône shows often disturbances, and its angular values may oscillate within rather wide limits. Furthermore: $q = \{011\}$, large and lustrous; $\omega = \{111\}$, small and lustrous; $s = \{021\}$, smaller and somewhat duller. The external form is elongated parallel the *c*-axis.
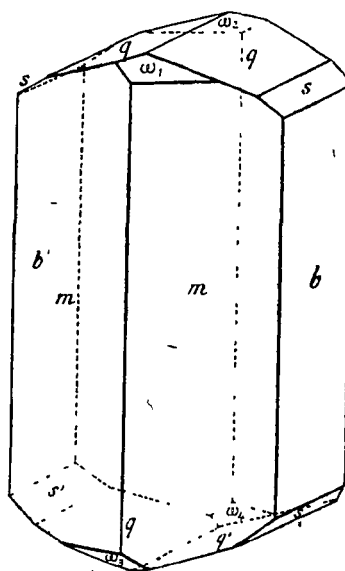
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[1]) F. M. JAEGER, Proceed. Kon. Acad. Amsterdam, **10**. 563. (1908): Zeits. f. Kryst. u Miner. **45**. 539. (1908).
[2]) C. S. HUDSON and D. H. BRAUNS, Journ. Amer. Chem. Soc. **37**. 1283, 2736. (1915).

Angles:		Observed:	Calculated:
$m:m = (110) : (1\bar{1}0) =$		* 52°38'	—
$q:q = (011) : (0\bar{1}1) =$		* 37 2	—
$m:b = (110) : (010) =$		63 41	63°41'
$q:b = (011) : (010) =$		71 29	71 27
$\omega:b = (111) : (010) =$		74 23	74 30
$\omega:m = (111) : (110) =$		52 59	52 56
$\omega:q = (111) : (011) =$		32 28	32 42
$\omega:m = (111) : (\bar{1}10) =$		68 42	68 33
$s:q = (021) : (011) =$		15 7	15 18
$s:m = (021) : (110) =$		75 44	75 43
$m:q = (110) : (211) =$		81 57	81 54½

Cleavable imperfectly parallel to {110}.

On m rectangular extinction.

§ 3. II. β-d-Fructose-penta-acetate.

This isomeric compound melts at 109° C.; its specific rotation in chloroform-solution is at 20° C. : $[\alpha]_D = -120°,9$; in benzene $[\alpha]$ is : $-105°,5$.

The crystals here described were obtained from a solution in ether;

Fig. 2.

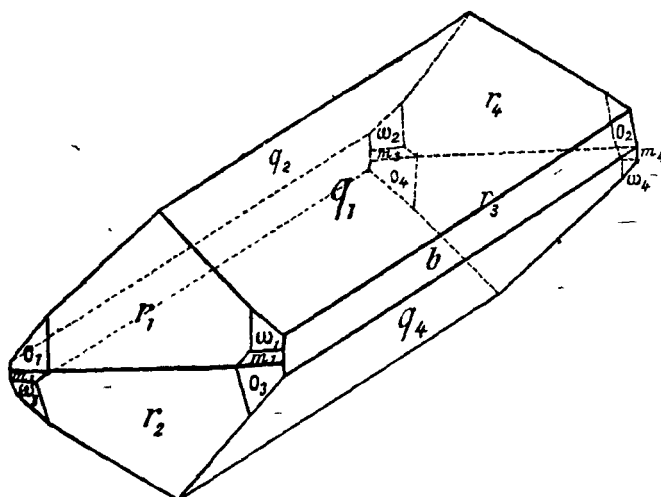β-d-Fructose-penta-acetate.

from benzene the substance crystallises in individuals containing 1 molecule of benzene.

Colourless, well-developed, prismatic crystals, which have a feebly bitter taste.

Rhombic-bisphenoidical.

$$a : b : c = 0,4941 : 1 : 0,9094,$$

Forms observed: $q = \{011\}$, very predominant, but yielding bad reflexes; $b = \{010\}$, smaller, much better reflecting than q; $r = \{101\}$,

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large and lustrous; $\omega = \{111\}$, small, but giving good reflexes; $o = \{1\bar{1}1\}$, larger than ω, but duller; $m = \{110\}$, very small, yielding sharp -images. The habit of the crystals is elongated parallel to the a-axis.

Angles:			Observed:	Calculated:
$b:q$	$= (010) : (011) =$ *		47°43′	—
$r:r$	$= (101) : (10\bar{1}) =$ *		57 2	—
$q:q$	$= (011) : (0\bar{1}1) =$		84 34	84°34′
$q:r$	$= (01\bar{1}) . (10\bar{1}) =$		69 16	69 19
$r:m$	$= (10\bar{1}) : (\bar{1}10) =$		37 58	38 1
$m:q$	$= (1\bar{1}0) : (0\bar{1}1) =$		72 36	72 39½
$q:o$	$= (011) : (111) =$		53 49	53 41½
$o \cdot o$	$= (1\bar{1}1) : (1\bar{1}\bar{1}) =$		72 22	72 37
$\omega \ m$	$= (111) : (110) =$		25 54	25 57
$m:o$	$= (110) : (11\bar{1}) =$		25 59	25 57
$b:o$	$= (010) : (11\bar{1}) =$		66 39	66 32
$b:\omega$	$= (0\bar{1}0) : (1\bar{1}1) =$		66 31	66 32
$o:\omega$	$= (1\bar{1}1) : (1\bar{1}1) =$		23 24	23 28
$b \cdot m$	$= (010) : (110) =$		63 55	63 42⅓

Perfectly cleavable parallel to $\{011\}$.

The plane of the optical axes is $\{100\}$, probably the c-axis is first bissectrix.

§ 4. From these measurements it is obvious that both isomerides possess *the same symmetry*, and, — within the limits of experimental errors, — *the same parameter $a : b$* ($= 0,4944$). Such relations are met with often in the case of polymorphic modifications of the same substance [1]. The identity of the cyclic structure in both molecules compels us to believe that it is this cyclic of atoms common to both, which determines the value of $a : b$. In no cases of polymorphism where up till now such analogy in the values of one of the parameter-ratios was observed, there could be indicated the existence of a reversible transition between the two modifications. In the case of α- and β-d-*Fructose-penta-acetates* too, as HUDSON and BRAUN demonstrate, no such reversibility seems to exist either (*monotropy*). It may seem probable that in cases like this, no ordinary polymorphism is present, but that in last instance the differences observed between such modifications are always caused by true *chemical isomerism*, in which a great part of the molecule is common to the two modifications.

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[1] F. M. JAEGER, Zeits. f. Kryst. u. Miner. **40**. 131. (1905) : thus in the case of α and β-1-3-4 *Dinitro diethyl-aniline* ; of α- and β-*Benzyl-phtalimide* (ibid. **40**. 371. (1905); of α- and β-*Mannite*, (GROTH's Chem. Kryst. **III**. 431. (1910); etc.